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<b>(21) International Application Number:</b> PCT/EP93/02073 <b>(22) International Filing Date:</b> 4 August 1993 (04.08.93)  <b>(30) Priority data:</b> 92202461.7 11 August 1992 (11.08.92) EP <i>(34) Countries for which the regional or international application was filed:</i> DE et al.  <b>(71) Applicant (for all designated States except US):</b> AGFA-GEVAERT NAAMLOZE VENNOOTSCHAP [BE/BE]; Septestraat 27, B-2640 Mortsel (BE).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> STEVENS, Marc, Petrus [BE/BE]; PLESSERS, Patrick [BE/BE]; VAN-COPPENOLLE, Gery [BE/BE]; Agfa-Gevaert N.V., Die 3800, Septestraat 27, B-2640 Mortsel (BE).		<b>(81) Designated States:</b> JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> OPAQUE POLYESTER FILM SUPPORT FOR PHOTOGRAPHIC MATERIAL		
<b>(57) Abstract</b>  A method of manufacture of photographic material comprising a polyolefin-voided biaxially orientated polyester film as a support and at least one light-sensitive silver emulsion layer is provided, characterised by the steps of: (i) providing on at least one side of a polyolefin-voided polyester film layer a layer of polyester film which is not voided by polyolefin (hereinafter referred to as a non-polyolefin voided layer), (ii) coating an aqueous primer or subbing layer to the side of said polyolefin-voided polyester film covered with said non-polyolefin voided layer, (iii) coating one or more hydrophilic layers onto the primer or subbing layer.		

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## OPAQUE POLYESTER FILM SUPPORT FOR PHOTOGRAPHIC MATERIAL

## 1. Field of the invention.

This invention relates to a method of manufacture of photographic material made from opaque voided polyester films and in particular to such films which may be used as paper substitutes in the photographic art.

## 2. Background of the Invention

The use of opaque voided polyester as a support that substitutes paper for a photographic print material is known from e.g. US-P 4,187,113 ; GB 1,563,591. It has been disclosed, in e.g. EP-A 455192, EP-A 289161, EP-A 332771, that opaque voided polyester can be advantageously used as a support for a thermal dye transfer receiver sheet.

US-P 4,187,113 describes the manufacture of a voided polyester film of the type comprising a polyester base containing between 3-27 % of polypropylene dispersed therein, which is biaxially orientated during processing to produce an opaque film having a light transmission of not in excess of 20 %.

Voided polyester films of the above type are strongly hydrophobic and will not form a strong bond with a hydrophilic photosensitive layer of the type used in the manufacture of photographic silver halide papers. It is known to treat the surface of a hydrophobic support with a primer coat by a process known as subbing in which a coating of at least one intermediate layer is put down on the support for anchoring the hydrophilic photosensitive layer(s) thereto.

It has been disclosed in US-P 4,187,113 that the polypropylene voided polyester can be treated after the biaxial stretching process or between stretching operations by coating with a first subbing layer of a vinylidene chloride polymer and a second subbing layer containing gelatin.

However, it has been found that primer layers, such as vinylidene chloride copolymers or polyester-polybutadiene copolymers, when coated from aqueous emulsions or dispersions do not spread evenly on the surface of the voided film.

In order to successfully coat a first subbing layer directly onto a surface of the voided polyester film it is necessary to coat from a solvent based solution of the copolymer or to treat the voided polyester with an oxidation plasma or corona.

The use of solvents gives rise to problems in production caused by the toxic nature of some solvents and the need to contain the solvent and prevent contamination of the atmosphere, and the disposal of waste solvent. Plasma treatment is only succesful at low pressure and is difficult to combine with an on-line film forming process.

The diffuse reflection of an opaque voided polyester support is relatively high. Such a high diffuse reflection is an undesirable property since it deteriorates the resolution (image sharpness) in the photographic print.

The need for an opaque voided polyester support for photographic print materials that can be subbed with water-based subbing layers and that gives high resolution in the photographic print is still not completely satisfied.

### 3. Objects and Summary of the Invention

It is an object of the present invention to provide a method to prepare an opaque voided polyester support for photographic materials that can be primed with aqueous primer solutions and allowing sharp images to be printed onto the photographic material.

It is another object of the present invention to provide a method to prepare an opaque voided polyester support for photographic materials that have a glossy appearance and that can be primed with aqueous primer solutions.

Other objects and advantages of the invention will become clear from the description hereinafter.

The above object is realized by providing a method of manufacture of a photographic material comprising a polyolefin voided biaxially orientated polyester film as support and at least one light-sensitive silver emulsion layer,

characterised by the steps of :

(i) providing on at least one side of a polyolefin-voided polyester film layer a layer of polyester film which is not voided by polyolefin (hereinafter referred to as a non-polyolefin voided layer)

(ii) coating an aqueous primer or subbing layer to the side of said polyolefin-voided polyester film covered with said non-polyolefin voided layer.

(iii) coating one or more hydrophilic layers on to the primer layer.

#### 4. Detailed Description of the Invention.

It is known, from e.g. US-P 4,187,113, that it is possible to provide sandwich structures comprising a layer of the opaque voided polyester film laminated with one or more layers of non-polyolefin voided films. Preferably said non-polyolefin voided film is an opaque film.

In EP-A 360201 a sandwich material comprising an opaque voided polyester film sandwiched between two non-polyolefin voided films that contain  $\text{TiO}_2$  has been described. The presence of non-polyolefin voided opaque layers on the outside of the sandwich improve the printability of the surface with an ink.

It has now been found that it was possible to dispense of organic solvents in applying a primer layer to a polyolefin voided polyester support when the polyolefin voided polyester is covered, before the application of the primer layer, with a non-polyolefin voided polyester layer. It was found that the covering of the polyolefin voided layer by such a non-polyolefin voided polyester layer not only made it possible to prime the support with an aqueous primer solution, but that the use of an opaque non-polyolefin voided layer, comprising a determined amount of opacifying agent, diminished the diffuse reflection of the support.

Preferably the polyolefin voided polyester film is sandwiched between two layers of non-polyolefin voided polyester, which may or may not be pigmented, to form a sandwich structure with a voided polyester core having a layer of non-polyolefin voided polyester on each side thereof.

Whilst in the preferred embodiment, the non-polyolefin voided polyester film is coextruded with the voided polyester film, pre-manufactured voided film and non-polyolefin voided film could be assembled together between hot rollers, before, after or between the biaxial stretching operations, or the non-polyolefin voided film could be extrusion coated onto voided polyester film before, between or after the biaxial stretching operations.

The polyester film is preferably made from a polyester which is the polycondensation product of terephthalic acid and ethylene glycol to produce a linear polymer containing between 70-140 repeating units. The film may be formed from other linear polyesters which are produced by condensing one or more dicarboxylic acids or a lower alkyl diester thereof, e.g., isophthalic, sulpho isophthalic, phthalic, orthophthalic, 2,5-, 2,6-, or 2,7-naphthalene dicarboxylic acid, succinic acid, sebacic acid, adipic acid, azelaic acid, bibenzoic acid, hexahydroterephthalic acid, or bis-p-carboxy phenoxy ethane, with one or more glycol, e.g. ethylene glycol, 1,3-propanediol, 1-4 butanediol, neopentyl glycol and 1,4-cyclohexane dimethanol. Mixtures of acids could be condensed with one or more glycols. The film can also be made of a blend of two or more polyester compositions.

The condensation product can be mixed with the polyolefin by several routes,

- a) the granulated polyester is dry blended with powdered or granulated polyolefin, and the mixed blend fed into the extruder, or
- b) the melt of the condensation product is fed into a melt extruder and the polyolefin is separately melted in an extruder and the polyolefin melt is then fed into the melt extruder to mix with the polyester melt. This route offers best results for uniform distribution of the polyolefin in the polyester.

The polyolefin may be a homopolymer or a copolymer of ethylene (high or low density) or of propylene. A mixture of homopolymers and copolymers may also be used. Preferably a homopolymer of propylene is used; an amount of 3-30 % by weight of total blend is mixed into the polyester, and more preferably about 10-20 % by weight of polypropylene. Amounts of polyolefin above 30 % lead to easy film rupture during production, and below 3 % there is little or no opacifying effect.

The polyolefin and polyester are mixed in the high shear extruder at about the melting point of the polyester and since the polyolefin and polyester are incompatible the polyolefin exists as discrete globules within the polyester continuous phase. The film opacity is produced when the film is stretched causing voids around the globules at the polyolefin/polyester interface. The polyolefin, preferably polypropylene, globules should be small to provide opacity and crease resistance and should generally have an average

diameter in the range of between 5-10 microns.

Simultaneously a second extruder melts the non-polyolefin containing, pigmented polyester and a third extruder melts the non polyolefin polyester.

The mixed polyester/polyolefin melt and the non-polyolefin containing, pigmented polyester (second extruder) or the mixed polyester/polyolefin melt and the non-polyolefin containing, pigmented polyester melt (second extruder) and the non-polyolefin polyester melt (third extruder) are coextruded through a feedblock and a one-slit die or through a multilayer die into a multilayer film. The resulting film sandwich may comprise the polyester/polyolefin containing layer as a core, surrounded by :

- (i) two pigmented non-polyolefin voided layers or
- (ii) one pigmented non-polyolefin voided layer and on the other side non pigmented a non-polyolefin voided layer or
- (iii) two non pigmented non-polyolefin voided layers.

After the die the multilayer film is rapidly quenched upon a casting drum as quickly as possible to produce a film in an amorphous state.

In a preferred embodiment of the invention a polyester/polyolefin voided film layer would have a polyester layer coextruded on each side thereof forming a sandwich construction having a voided polyester core with a non-polyolefin voided layer on each side.

In another embodiment, the outer layer could be voided by barium sulphate.

The outer polyester layers may be, but not necessarily, formed from the same polyester as the base material of the core layer. The non-polyolefin voided polyester may be more amorphous than the polyester of the core layer to improve the crease resistance. The outer layers may have the same or different compositions.

The combined film layers are then biaxially oriented by stretching in one direction and then in a second direction. The extruded combined film layers will have a thickness of approximately 500 to 2000  $\mu\text{m}$  and are first stretched longitudinally in the direction of extrusion. The longitudinal stretching ratio should be sufficient to create voids. Stretching is preferably done at a temperature above but close to the glass transition temperature of the polyester in order to improve opacity. The preferred stretch ratio is about between 3 and 4.

The longitudinal stretching operations known in the art to produce biaxially oriented polyester film may be used. For instance, combined film layers are passed between a pair of infra red heaters which heats the layers to a temperature above the glass transition temperature of the polyester (about 80°C for polyethylene terephthalate) in the region where the stretching occurs.

By longitudinal stretching voids are produced at the polyester/polyolefin interface in the polyester/polyolefin layer extending longitudinally from each polyolefin globule.

After the longitudinal stretching the film sandwich is cooled to allow for further treatment between longitudinal and transverse stretching e.g. allowing for the coating by a primer layer.

Then the combined layers are then passed through hot air heaters and the film heated above the glass transition temperature for transverse stretching by means of a tenter apparatus. The stretch ratio in the transverse direction is preferably between 3 and 4. The transverse stretching of the film causes the voids to extend transversely of each polyolefin globule.

The biaxially stretched combined film layers are passed through a second set of hot air heaters which blow hot air at a temperature of between 160 and 240 degrees Centigrade onto the film layers to heat set the film layers. The heat set temperature must be sufficient to obtain crystallization of the polyester but care must be taken not to overheat the layers since the voids can collapse. On the other hand increasing the heat set temperature improves the crease resistance of the film. A compromise of the properties depending upon heat set temperatures must be chosen.

Instead of subsequent stretching it is also possible to stretch the film sandwich simultaneously in both directions.

A first aqueous subbing layer, called primer layer, may be applied to the support after the biaxial stretching. It is also possible, according to this invention to apply the aqueous primer layer before or after longitudinal stretching. Preferably the first aqueous primer layer is applied to the support between the two stretching operations. The aqueous primer layer may be applied to the polyester layer by a coating means such as an air knife coating system. The first subbing layer (primer layer) is for example formed from a chloride containing copolymer such as vinylidene chloride copolymer in latex form having some hydrophilic functionality through the presence of a copolymerized unsaturated



carboxylic acid which is applied as an aqueous dispersion. Also, polyester/polybutadiene copolymers as disclosed in European Patent application No. 922005939 may be used. An antistatic primer layer as described e.g. in European non-published application 92203978.9 can also advantageously be used in the preparation of the support according to the present invention.

Any other primer or subbing layer(s) can be applied from aqueous latex dispersions that are known in the art for improving the adhesion of hydrophilic colloid coatings e.g. gelatin layers to polyester supports.

A second aqueous subbing layer usually containing gelatin in admixture with a hydrophobic latex-copolymer e.g. a butadiene/acrylonitrile copolymer and preferably also colloidal silica, can be applied to the primer layer by for instance a cascade coating apparatus. The coated film layers may then be cut-to-width and are coated either before or after cutting with a light-sensitive gelatin silver halide emulsion layer and other photographic auxiliary layers.

Additives may be added to the sandwich of a polyolefin voided polyester film between non-polyolefin voided polyester layers. Most specifically additives which are only or most functional at the surface of the film support may be added to the outer layers. This procedure allows for a reduction in the total addition of additive with the same or better functional result than adding the additive to the core layer.

It has been found that the image sharpness of a photographic material coated on such a sandwich enhanced, by adding  $\text{TiO}_2$  to the non-polyolefin voided polyester layer. It was found that the addition of  $\text{TiO}_2$  in amounts between 10 and 25 % w/w to the non-polyolefin voided polyester film layers gave the beneficial result on image sharpness without giving too high weight to the non-polyolefin voided layer. In a more preferred embodiment of this invention 15 to 20 % w/w of  $\text{TiO}_2$  is added to the non-polyolefin voided layers. By the addition of  $\text{TiO}_2$  the opacity of the support is increased to 96 % or more, which is highly desirable for photographic print material.

$\text{SiO}_2$  can be added to give the material a good writing surface. Anti-static agents can be added in the outer layers to improve the electrical properties. The appearance and brightness can be improved by adding fluorescent brighteners, pigments and/or coloured

compounds in the outer layer.

The final multilayer material may have a voided layer having a thickness T1 of 75-300  $\mu\text{m}$  and a non-voided layers of a thickness T2 of between 1 and 50 and preferably between 5 and 20  $\mu\text{m}$ .

A photographic silver halide emulsion material comprising a support according to the present invention as defined hereinbefore may contain (a) silver halide emulsion layer(s) of any type known to those skilled in the art. For example, these materials may contain a silver halide emulsion layer of the type used in continuous tone or halftone photography, microphotography, radiography and films for graphic arts application. The defined support can be used most advantageously in black-and-white or colour photographic print materials.

For the composition of silver halide emulsion layers reference is made e.g. to Research Disclosure 17,643 of December 1978 and Research Disclosure 307,105 of November 1989.

A photographic silver halide emulsion material comprising a support according to the present invention as defined hereinbefore may comprise, apart from (a) silver halide emulsion layer(s), antistatic layers as described in e.g. EP-A 440957, European non published application 92203149.7, European non published application 92200230.8, US-P 4,495,276, and EP-A 191302 ; also antihalation layers, backing layers, intermediate layers and protective layers may be present.

#### EXAMPLES

Various supports according to the present invention were prepared.

The parameters investigated were :

1. The melt flow of the core (polyolefin voided) layer in kg/hour
2. The melt flow of the outer (non-polyolefin voided) layers in kg/hour
3. The longitudinal stretch stress in  $\text{N/mm}^2$
4. Heat-setting
5. The thickness of the outer layers
6. Total thickness of the sandwich of core and outer layers
7. Concentration of  $\text{TiO}_2$  in the outer layers (% w/w)

The sample were evaluated in terms of :

1. Opacity
2. Picture sharpness
3. Creasing resistance

Table 1 gives all examples 1 to 11 the values of parameters 1 to 4 and table 2 gives the values of parameters 5 to 7 and test data 1 to 3 for the film supports described herein coated with photosensitive and auxiliary layers as used for photographic print paper.

The sandwich constructions comprising a core layer of 85% by weight polyethylene terephthalate voided by 15% by weight polypropylene having a melt flow index of 3 (ASTM D1238), with outer layers of polyethylene terephthalate having  $\text{TiO}_2$  (anatase form) filler of various concentrations as shown. The  $\text{TiO}_2$  has a particle size of 0.2-0.3  $\mu\text{m}$ .

The polyester layers were extruded at 270-280 degrees centigrade at differing melt flows depending upon the thicknesses of the final layers and with an initial total extrudate thickness of 1100  $\mu\text{m}$ .

The extrudate was drawn down with longitudinal stretching ratio of 3.3 and longitudinal stresses as shown in the tables and transverse stretching ratio of 3.0 at a temperature of 100 degrees centigrade and at stretching speed of 1000% per minute to give final total film thicknesses as shown in table 2. Only examples 9-11 were heat set. Between longitudinal and transverse stretching an aqueous primer layer was applied pro rata of 130 sq.m. per litre from the following composition :

30 % wgt aqueous dispersion of co(vinylidene chloride/methylacrylate/itaconic acid) (88/10/2 wgt %)	246 ml
demineralised water	665 ml
36 % wgt per volume aqueous silica (Kieselcol 100F of Bayer AG)	48 ml
alkali to raise pH to 8.2	
coating aids.	

This aqueous coating composition spreads well on the non-voided polyester layer whereas it could not be applied to a voided polyester film only. It adhered well before as well as after stretching.

After transverse stretching the following subbing layer composition was applied pro rata of 30 sq.m. per litre :

demineralised water

950 ml

gelatine

11.4 g

36 % wgt per vol. aqueous silica

28.4 ml

(Kieselsoil 300F of Bayer AG)

coating aids.

TABLE 1

Example n°	Melt flow core layer (kg/hour)	Melt flow outer layer (kg/hour)	Longitudinal stretch stress (N/mm <sup>2</sup> )	Heat Set T °C
1	115	29	2.6	no
2	115	31	3.8	no
3	124	31	4.0	no
4	124	32	3.8	no
5	208	25	3.9	no
6	124	31	3.8	no
7	36	28	3.9	no
8	90	31	3.2	no
9	90	31	3.2	160
10	90	31	3.2	180
11	90	31	3.2	200
12	160	38	4.0	188
13	160	38	3.7	172

TABLE 2

Exam N°	Thickness outer layer $\mu\text{m}$	Total Thickness $\mu\text{m}$	TiO <sub>2</sub> % w/w	Opacity (1) %	Resol (2)	Crease (3)
1	10	273	5	97.5	K0	20
2	10	263	10	98.0	K2	20
3	10	253	15	98.5	K4	20
4	10	231	20	98.0	K4	8
5	5	200	10	97.0	K2	10
6	10	201	10	97.0	K2	8
7	30	254	15	96.5	K4	16
8	13	178	10	95.0	K1	8
9	13	141	10	92.0	K1	6
10	13	151	10	93.5	K1	4
11	13	148	10	92.0	K1	4
12	10	160	15	98.2	K4	3
13	10	160	15	98.0	K4	3

(1) The opacity is measured as described by test T425m-60 published by TAPPI, 360 Lexington Ave, New York, USA.

(2) Image resolution : Exposure through a lattice of 8 lines/mm.

Evaluation :

K4 = excellent

K3 = very good

K2 = good

K1 = poor

K0 = bad.

Conventional polyethylene-coated paper for photoprints (Agfa CN-310 paper) has an evaluation of K3.

(3) Crease resistance

Test procedure : bending the film support (without emulsion

layers) over rolls of 3-4-6-8-10-12-14-16-18 and 20 mm diameter. The smallest roll whereby no creasing is noticed is given.

For conventional polyethylene-coated paper (Agfa CN-310)  $\leq 6$ .

The addition of  $\text{TiO}_2$  in an amount of 15 to 20 % w/w gives a large improvement of picture sharpness, the sharpness gets even better than that of photographic materials coated on conventional polyethylene-coated paper. Heatsetting increased the crease resistance but lowers the opacity.

## CLAIMS

1. A method of manufacture of photographic material comprising a polyolefin voided biaxially oriented polyester film as support and at least one light-sensitive silver emulsion layer,

characterised by the steps of :

(i) providing on at least one side of a polyolefin-voided polyester film layer a layer of polyester film which is not voided by polyolefin (hereinafter referred to as a non-polyolefin voided layer)

(ii) coating an aqueous primer or subbing layer to the side of said polyolefin-voided polyester film covered with said non-polyolefin voided layer

(iii) coating one or more hydrophilic layers on to the primer or subbing layer.

2. A method as claimed in claim 1, characterised in that said non polyolefin voided layer comprises 10 to 25 % of  $\text{TiO}_2$ .

3. A method as claimed in claim 2, characterised in that said non polyolefin voided layer comprises 15 to 20 % of  $\text{TiO}_2$ .

4. A method as claimed in claims 1 or 2, characterised in that the layers of non-polyolefin voided polyester are coextruded with the layer of voided polyester.

5. A method according to claims 1 to 3, characterised in that two layers of non-polyolefin voided polyester are coextruded with the voided polyester layer for forming a sandwich structure with a voided polyester core having a layer of non-polyolefin voided polyester one each side thereof.

6. A method of manufacture according to any one of claims 1 to 5, characterised in that said layers of voided and non voided polyester are biaxially stretched and the aqueous primer or subbing layer composition is applied between the two stretching operations.

7. A method as claimed in claim 6 characterised in that the longitudinal stretch ratio is about between 3 and 4.

8. A method of manufacture as claimed in claim 6, characterised in that after the application of the said subbing layer and the subsequent stretching of the voided and non-voided polyester layers in the second axial direction, the whole film is heat set so that the subbing layer is heat set to its adjacent polyester layer.

9. A method as claimed in any of the preceding claims, characterised in that said layer(s) of non-polyolefin voided film is (are) 1-30  $\mu\text{m}$  thick.

10. A method as claimed in any one of claims 1 to 9, characterised in that the non-polyolefin voided layer is a non-voided layer.

11. A method as claimed in any one of claims 1 to 10, characterised in that the polyolefin voided polyester layer has polyolefin globules therein with diameters of between 5 to 10  $\mu\text{m}$ .

12. A method as claimed in any one of claims 1 to 11, characterised in that the said primer or subbing layer comprises a copolymer of vinylidene chloride.

13. A method as claimed in any one of claims 1 to 11, characterised in that the said primer or subbing layer comprises a copolyester.

14. A method as claimed in any one of claims 1 to 13, characterised in that the layer of voided polyester film comprises a linear polyester formed from the condensation of terephthalic acid and ethylene glycol having a number average degree of polymerisation of 70-140, and about 10-20 % by weight of polypropylene homopolymer.



## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 93/02073

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 G03C1/795 G03C1/93

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 G03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 360 201 (DIAFOIL COMPANY LIMITED) 28 March 1990 see page 5, line 28 - line 36; claim 1 ---	1-14
Y	US,A,4 255 516 (K KATOH ET AL) 10 March 1981 see column 7, line 8 - line 48 ---	1-14
Y	GB,A,718 422 (E.I.DU PONT DE NEMOURS AND CO.) 17 November 1954 see the whole document ---	1-14
Y	EP,A,0 376 693 (KONICA CORPORATION) 4 July 1990 see page 2, line 4 - line 6 see claims 1,9 --- -/--	13

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 187 113 (C F MATHEWS) 17 November 1954 cited in the application see column 5, line 1 - line 42 ---	1-14
A	EP,A,0 228 041 (GENERAL ELECTRIC COMPANY) 8 July 1987 see page 3, line 9 - line 12 -----	1

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